Excited State Intramolecular Proton Transfer with Nuclear–Electronic Orbital Ehrenfest Dynamics

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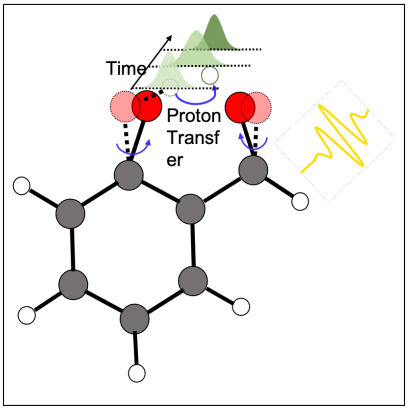
Abstract

The recent development of the Ehrenfest dynamics approach in the nuclear-electronic orbital (NEO) framework provides a promising way to simulate coupled nuclear-electronic dynamics. Our previous study showed that the NEO-Ehrenfest approach with a semiclassical traveling proton basis method yields accurate predictions of molecular vibrational frequencies. In this work, we provide a more thorough analysis of the semiclassical traveling proton basis method to elucidate its validity and convergence behavior. We also conduct NEO-Ehrenfest dynamics simulations to study an excited state intramolecular proton transfer process. These simulations reveal that nuclear quantum effects influence the predictions of proton transfer reaction rates and kinetic isotope effects due to the intrinsic delocalized nature of the quantum nuclear wave function. This work illustrates the importance of nuclear quantum effects in coupled nuclear-electronic dynamical processes and shows that the NEO-Ehrenfest approach can be a powerful tool to provide insights and predictions for these processes.

Graphical TOC Entry



Dynamical processes, such as excited state proton transfer (ESPT)[1,2] and proton-coupled electron transfer (PCET),[3–6] have led to a number of phenomena of great scientific and technological interest, including bio-imaging,[7,8] fluorescent probes,[9,10] and organic light-emitting diodes.[2] ESPT can also provide a useful framework for understanding the binding properties of proteins.[11,12] Additionally, PCET is a key step of numerous biological processes, such as photosynthesis, respiration, and reactions in light-harvesting devices.

Since the fundamental driving force underlying these processes is the quantum mechanically coupled electrons and protons, it is essential to use a theoretical method that can accurately treat the dynamical interplay between electronic and protonic degrees of freedom. This necessity has led to the development of a variety of different non-adiabatic dynamics approaches, including Ehrenfest dynamics,[13–15] surface hopping,[16–18] *ab initio* multiple spawning,[19,20] multi-configurational time-dependent Hartree,[21,22] and Gaussian wave packet dynamics.[23,24] The recent development of the Ehrenfest dynamics approach[25] based on the nuclear-electronic orbital (NEO)[26–30] framework offers a novel angle for tackling the coupled nuclear-electronic dynamics. Within this approach, specified nuclei (typically protons) are treated quantum mechanically on equal footing with electrons without relying on the Born-Oppenheimer (BO) approximation. In this way, the non-adiabatic couplings between the electrons and the specified nuclei are naturally included, and the explicit evaluation of the non-adiabatic coupling vector is therefore avoided. Moreover, the fully quantum mechanical treatment of specified nuclei in the NEO-Ehrenfest approach allows it to describe crucial nuclear quantum effects that could make meaningful differences in dynamical processes, such as zero-point energy, quantized vibrational levels, and tunneling.

Our initial study of the NEO-Ehrenfest approach[25] focused on establishing the theoretical foundation. A semiclassical travelling proton basis (TPB) was introduced to improve the accuracy for a given proton basis set and to account for the difficulty of a localized proton basis set to describe extensive proton motion. The accuracy of this TPB approach was supported by benchmark studies of molecular vibrational frequencies.[25] However, the major purpose

of developing the NEO-Ehrenfest method is to study how nuclear quantum effects influence proton transfer dynamics in processes such as ESPT and PCET. In these cases, the transferring proton travels relatively long distances, and a substantial set of proton basis functions centered at a fixed position would be required to describe the full trajectory, making proton transfer processes significantly more challenging than the prediction of vibrational frequencies. However, our previous application of the semiclassical TPB approach to vibrational frequencies did not demonstrate the accuracy of the method for cases involving extended proton motion. This Letter aims to address this important issue by first benchmarking the semiclassical TPB approach with model harmonic and anharmonic potentials. Having established the validity of the semiclassical TPB approach, we present the first application of the NEO-Ehrenfest method for simulating an ESPT process in the *o*-hydroxbenzaldelhyde (oHBA) molecule. The success of the semiclassical TPB approach in the studied ESPT process opens a variety of possibilities for simulating nonequilibrium proton transfer processes within the NEO framework.

In the NEO-Ehrenfest method, the dynamics of the electronic density matrix is governed by the Liouville-von-Neumann equation,

$$i\frac{\partial}{\partial t}\mathbf{P}^{\mathrm{e}} = [\mathbf{F}^{\mathrm{e}}, \mathbf{P}^{\mathrm{e}}] \tag{1}$$

in which $\mathbf{P}^{\mathrm{e}}$ and $\mathbf{F}^{\mathrm{e}}$ are the electronic density matrix and Fock matrix in the orthogonalized basis. The classical nuclei follow Newtonian dynamics:

$$\ddot{\mathbf{R}}_N = -\frac{1}{m_N}\boldsymbol{\nabla}_{\mathbf{R}_N} E \tag{2}$$

in which $\mathbf{R}_N$ and m_N are the position and mass, respectively, of the Nth classical nucleus, and E is the total energy. In contrast, the dynamics of the protonic density matrix with a

semiclassical TPB are governed by the following equation of motion,

$$
\begin{aligned}
i\frac{\partial}{\partial t}\mathbf{P}^{\mathrm{p}} &= [\mathbf{F}^{\mathrm{p}}, \mathbf{P}^{\mathrm{p}}] - i\left(\boldsymbol{\tau}\mathbf{P}^{\mathrm{p}} + \mathbf{P}^{\mathrm{p}}\boldsymbol{\tau}^{\dagger}\right) \\
\ddot{\boldsymbol{\mathcal{R}}} &= -\frac{1}{m}\boldsymbol{\nabla}_{\boldsymbol{\mathcal{R}}} E
\end{aligned}
\tag{3}
$$

in which $\mathbf{P}^{\mathrm{p}}$ and $\mathbf{F}^{\mathrm{p}}$ are the protonic density matrix and Fock matrix in the orthogonalized basis. For typical molecular implementations, each quantum proton is represented by electronic and protonic basis functions with the same centers that are assumed to move together. The $\boldsymbol{\tau}$ matrix carries information of the protonic basis set time derivative. $\boldsymbol{\mathcal{R}}$ and m are the proton basis function center, which is distinct from the classical nuclear positions, and the proton mass, respectively. In these equations, $\mathbf{F}^{\mathrm{e}}$ includes terms corresponding to the kinetic energy of the electrons, electron-electron Coulomb and exchange interactions, Coulomb interactions between the electrons and quantum protons and between the electrons and classical nuclei, and electron-electron and electron-proton correlation. $\mathbf{F}^{\mathrm{p}}$ includes the analogous terms for the quantum protons. Moreover, $\mathbf{F}^{\mathrm{e}}$ and $\mathbf{F}^{\mathrm{p}}$ each depend on both $\mathbf{P}^{\mathrm{e}}$ and $\mathbf{P}^{\mathrm{p}}$. The total energy E is the expectation value of the NEO Hamiltonian with respect to the product of the electronic and protonic determinants, where the NEO Hamiltonian includes the kinetic energies of the electrons and quantum protons and all Coulombic interactions between the electrons, quantum protons, and classical nuclei. The detailed expressions for $\mathbf{P}$, $\mathbf{F}$, $\boldsymbol{\tau}$, E and the energy gradients can be found in our initial NEO-Ehrenfest study.[25]

The semiclassical TPB approach adjusts the proton basis function positions automatically, in a classical manner, as the proton density matrix propagates in time. It is capable of exploring a larger region of configuration space compared to a fixed proton basis (FPB) and therefore allows the use of a smaller protonic basis set. When computing molecular vibrational frequencies, such a capability allows it to yield much more accurate results compared with the FPB approach for a given basis set, as illustrated by our previous study.[25] Note that we do not use the traveling basis equation of motion for the electronic density because there is a sufficient number of electronic basis functions to describe electronic fluctuations.

The semiclassical TPB approach has a number of advantages. It is simple to implement, numerically stable, and will converge to the exact results as the basis set approaches completeness. To benchmark the quality of the TPB approach, in Figures 1 and 2 we compare the time evolution of a proton wave function in harmonic and Morse potentials (see the Supporting Information for the detailed expressions) between the semiclassical TPB approach and the exact results obtained on a grid. In both cases, we find that the semiclassical TPB approach is capable of producing nearly exact predictions compared to those solved on a numerical grid. In contrast, the trajectory with the FPB approach, where a single set of basis functions is centered at the initial position, deviates from the exact results by a noticeable amount, especially in the case of a Morse potential. We also find the error in the predicted proton position expectation value grows with time for the FPB approach. In contrast, the error of the TPB approach remains constant during the simulated time duration. However, despite the observation that the semiclassical TPB approach generates accurate trajectories in terms of the evolution of the proton position expectation values, it does not strictly conserve energy, unlike the dynamics solved on a grid or the FPB approach. As demonstrated in the Supporting Information, the semiclassical TPB approach is not expected to rigorously conserve energy, especially with small basis sets, although the energy conservation error can be reduced by increasing the size of the basis set, as shown in Figure S2. However, numerical tests carried out here suggest that the trajectory does not deviate much from the exact solution despite the lack of exact energy conservation.

A more difficult problem is the symmetric double-well potential. Its high anharmonicity produces dynamics that are different from classical mechanics. Since the left and right wells are symmetric, the ground state wave function should contain equal density contributions from both wells. Therefore, a large number of basis functions is usually required to ensure that the space spanned by them is large and flexible enough to form such a state. In Figure 3 we show the results of the semiclassical TPB and FPB approaches for a symmetric double well potential. With a small basis (PB5-F, 5s4p3d2f),[31] we observe that although

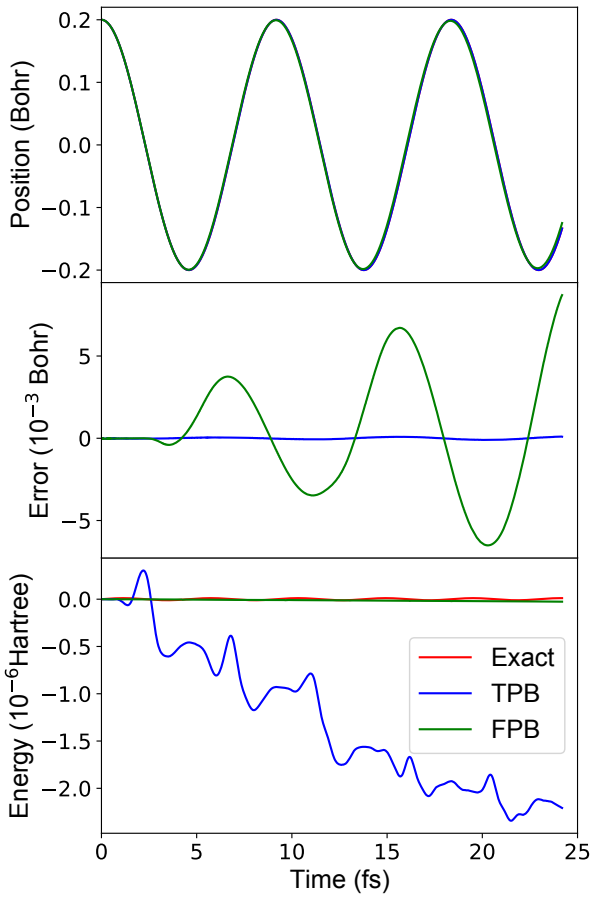


Figure 1: Time evolution of the proton position expectation value (top), error with respect to the exact solution in proton position expectation value for TPB and FPB (middle), and energy conservation (bottom) with harmonic potential. The semiclassical TPB approach and the FPB approach using the PB4-F2[31] (4s3p2d2f) basis are compared to each other and to the exact results obtained on a grid.

the semiclassical TPB approach is capable of capturing the basic trend of the time evolution of the proton position, it does not provide quantitative accuracy. As expected, the FPB approach deviates from the exact dynamics by a considerable amount. With a larger proton basis (PB6-F, 6s5p4d3f),[31] both the TPB and FPB trajectories are improved, and we start to observe the convergence behavior toward the exact results. This test suggests that large proton basis sets should be used when the proton wave function is more delocalized to ensure converged dynamical behavior.

With a better understanding of the merits and drawbacks of the semiclassical TPB ap-

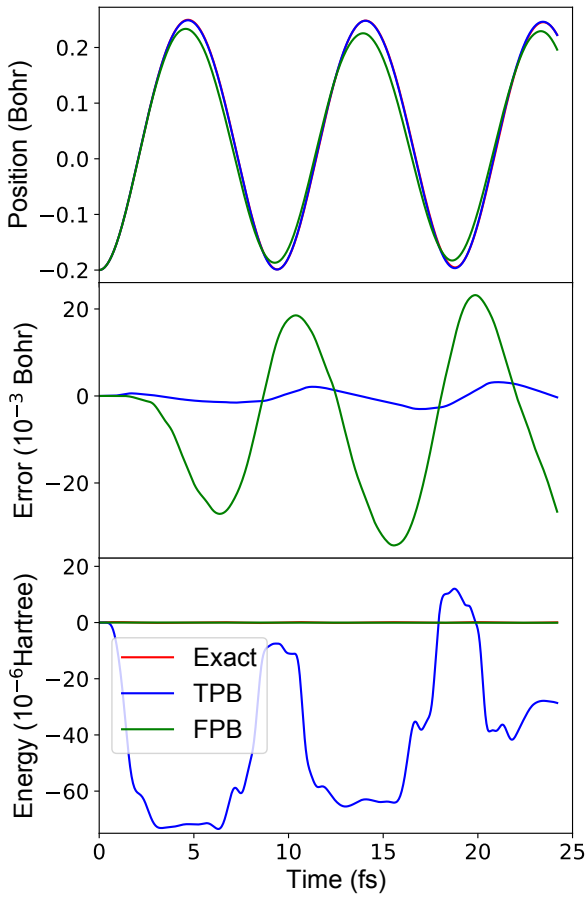


Figure 2: Time evolution of the proton position expectation value (top), error with respect to the exact solution in proton position expectation value for TPB and FPB (middle), and energy conservation (bottom) with Morse potential. The semiclassical TPB approach and the FPB approach using the PB4-F2[31] (4s3p2d2f) basis are compared to each other and to the exact results obtained on a grid. The energies of the exact and FPB trajectories are virtually indistinguishable on this plot.

proach, we now use NEO-Ehrenfest dynamics to study the ESPT process in the oHBA molecule. oHBA is the smallest aromatic molecule displaying ESPT, and it has been subject to numerous theoretical[32,33] and experimental[34] investigations. The potential energy surface predicted by time-dependent density functional theory (TDDFT) and coupled cluster methods show that the proton transfer occurs without any energy barrier on the $S_1(\pi\pi^*)$ excited state. This finding is corroborated by time-resolved photoelectron spectroscopy, which demonstrates that the proton transfer occurs in less than 50 fs. *Ab initio* calculations[33] also revealed that backbone displacement is required for the barrierless proton transfer in this

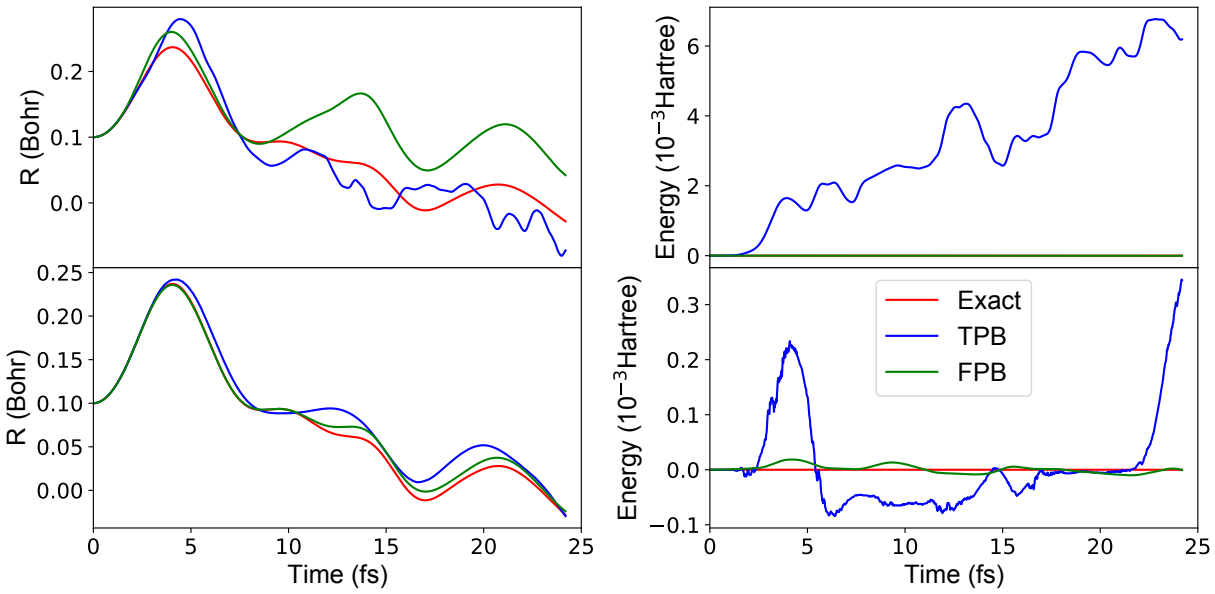


Figure 3: Time evolution of the proton position (left) and energy conservation (right) for the symmetric double well potential using different protonic basis sets, comparing the semiclassical TPB, FPB, and exact results. The upper panel uses the PB5-F basis (14 functions), and the lower panel uses the PB6-F basis (18 functions).

ESPT process. Specifically, in order for proton transfer to occur on the excited state, the donor oxygen (O_D) and acceptor oxygen (O_A) must be at a closer distance compared to their ground state configuration.[28]

To simulate ESPT using NEO-Ehrenfest dynamics, at $t = 0$ fs we prepare the initial state that corresponds to a vertical excitation from the ground state to the first excited electronic state at the ground state equilibrium geometry. This process is modeled by swapping the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which gives rise to an $S_0 \rightarrow S_1$ excitation. The excitation energy predicted in this way is 4.51 eV, which is overestimated compared to the prediction of 3.97 eV from linear-response TDDFT. This overestimation is mainly due to the neglect of contributions from other orbitals to the excitation. However, linear-response TDDFT indicates that the HOMO→LUMO transition represents 95% of the excitation. Therefore, the simple HOMO/LUMO swapping provides a qualitatively correct description of the excited state.

The cc-pVDZ[35] and PB4-F2 basis sets are used for the electrons and the quantum proton,

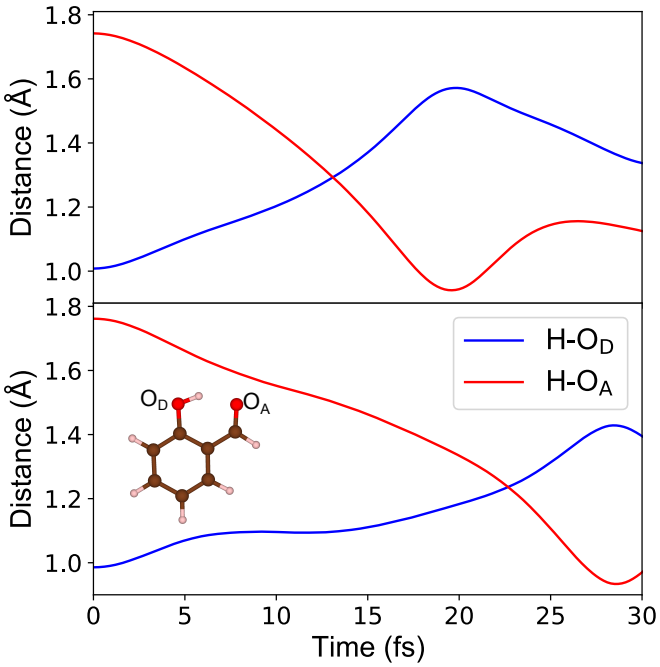


Figure 4: Distance from the transferring proton to the donor oxygen (O_D) and the acceptor oxygen (O_A) as a function of time for ESPT in oHBA with (top) NEO-Ehrenfest and semiclassical TPB approach and (bottom) Ehrenfest in which all nuclei are treated classically.

respectively. Electron exchange and correlation are modeled by the B3LYP functional,[36–38] and electron-proton correlation is described with the epc17-2 functional.[39] The initial momentum is set to be zero in all directions for all atoms. The time evolution of the distance between the transferring proton and the donor and acceptor oxygen atoms, O_D and O_A, is shown in Fig. 4, comparing the results obtained using NEO-Ehrenfest (top) and Ehrenfest with all nuclei treated classically (bottom). Distances that involve the quantum proton are computed using the proton position expectation value. In order to illustrate the necessity of using the TPB, we show that no PT is predicted if a single fixed proton basis center that is initially placed near the donor oxygen is used (see Figure S3). On the other hand, if a set of four fixed proton basis function centers spanning the proton transfer pathway is used, the proton transfer dynamics is similar to that observed with the semiclassical TPB method, providing further validation for the TPB scheme (see Figure S6).

The proton transfer time can be defined as the time at which the H-O_D and H-O_A

distances are equal (i.e., when the two curves cross). This proton transfer time is predicted to be $t = 13.10$ fs with NEO-Ehrenfest and $t = 22.68$ fs with classical Ehrenfest, which refers to Ehrenfest dynamics with all nuclei treated classically. This result suggests that treating the transferring proton quantum mechanically significantly decreases the proton transfer time. This behavior can be understood by considering the delocalized nature of the quantum proton. For proton transfer to occur, O_D and O_A must first get closer compared to their separation in the ground state equilibrium structure. As the delocalization associated with the quantum proton wave function allows it to span a larger region of space than a classical proton, this delocalization substantially reduces the distance that these two oxygen atoms must travel. This interpretation is supported by the the time evolution of the O_D-O_A distance shown in Fig. 5, where the proton transfer times are indicated with vertical dashed lines. This figure illustrates that proton transfer occurs at a longer O_D-O_A distance with NEO-Ehrenfest (2.57 Å) than with classical Ehrenfest (2.42 Å).

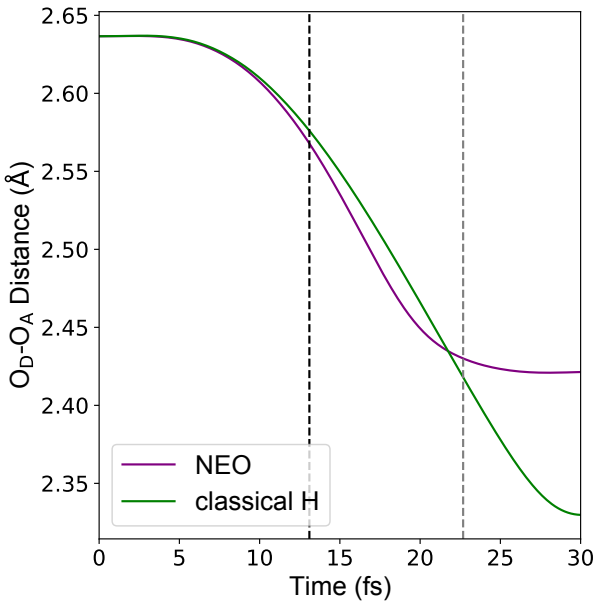


Figure 5: Distance between the O_D and O_A atoms as a function of time for ESPT in oHBA simulated using (purple) NEO-Ehrenfest dynamics with semiclassical traveling proton basis and (green) Ehrenfest dynamics in which all nuclei are treated classically. Vertical dashed lines show the times at which the H-O_D and H-O_A distances are equal for the corresponding methods.

We now investigate the kinetic isotope effect (KIE) for this ESPT by replacing the transferring proton with deuterium in both the NEO and classical Ehrenfest simulations. In Table 1, we show the comparison of the hydrogen transfer time for protium and deuterium, along with the O_D-O_A distances at the times of hydrogen transfer. The KIE is computed as the ratio between the deuterium and protium transfer times. Table 1 shows that the quantum treatment of the transferring nucleus leads to a larger KIE compared to the classical description. The KIE in the classical limit is directly governed by the change in particle mass, which usually leads to slower reaction dynamics for the heavier atom. For quantum dynamics, switching from protium to deuterium not only doubles the particle mass, but it also drastically reduces the delocalization of the nuclear wave function. As discussed previously,[40] the extent of the wave function delocalization can modulate the protium/deuterium transfer. The decrease in wave function delocalization in deuterium requires a smaller O_D-O_A distance (2.50 Å vs. 2.57 Å) for deuterium transfer than for protium transfer, leading to a longer reaction time. The combination of increased mass and decreased wave function delocalization for deuterium results in a larger KIE in NEO-Ehrenfest dynamics. It is also worth noting that although the hydrogen transfer dynamics is slowed down by switching from protium to deuterium, the rate difference is not as great as in those dynamics where the transfer is driven by proton tunneling.[40,41] Since this ESPT process is barrierless, this moderate effect is expected.

Table 1: Comparison of Hydrogen Transfer Time (fs) and O_D-O_A distance (Å) between NEO and Classical Ehrenfest Dynamics for Protium and Deuterium Transfer.

	Time(H)	O_D-O_A(H)	Time(D)	O_D-O_A(D)	KIE
NEO	13.10	2.57	18.94	2.50	1.44
Classical	22.74	2.42	28.30	2.35	1.24

This Letter extends the theoretical foundation of the NEO-Ehrenfest dynamics approach with a focus on the validity of the semiclassical traveling basis method. Although the semi-

classical TPB method produces a larger amount of energy conservation error compared with FPB, it has been demonstrated with model potentials to be capable of producing accurate trajectories. By comparing the trajectories obtained with NEO-Ehrenfest and Ehrenfest with classical nuclei, we showcase two significant effects of the quantum hydrogen nucleus on the ESPT dynamics in oHBA. First, the proton transfer reaction is accelerated due to the delocalization of the proton wave function, which results in a shorter minimum traveling distance for the donor and acceptor atoms in the molecular backbone. Second, the KIE is increased compared to the classical simulations because switching from protium to deuterium not only increases the particle's mass, but also reduces the extent of its wave function delocalization, requiring longer distances for the donor and acceptor atoms in the molecular backbone to travel. These studies illustrate that the NEO-Ehrenfest approach can be a powerful tool to simulate proton transfer dynamics with full incorporation of the nuclear quantum effects of the transferring proton. It paves the way for future studies of more complicated reactions involving multiple protons, solvent effects, and tunneling. Research in these exciting directions are underway.

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Supporting Information Available: The supporting information includes: computational details; detailed expressions for electron and proton Fock matrices; proof that the semiclassical traveling proton basis does not necessarily conserve energy with an incomplete basis, along with its exactness in the limit of a complete basis; comparison of energy conservation and proton transfer trajectories for the oHBA ESPT simulation using different protonic basis sets and using one fixed protonic basis function center, one traveling protonic basis function center, and a set of four fixed protonic basis function centers.

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